PREPARATION OF TRIMETHYLOXOSULFONIUM-^{13}C IODIDE

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SUMMARY

Trimethyloxosulfonium-^{13}C iodide (30% ^{13}C-enriched) was prepared from ^{13}C-labelled barium carbonate by proceeding through methanol-^{13}C and methyl-^{13}C iodide. The original procedure for the preparation of trimethyloxosulfonium iodide which afforded 53.6% of product was modified so that a 77% yield of trimethyloxosulfonium-^{13}C iodide was obtained.

Key Words: Trimethyloxosulfonium-^{13}C iodide, Corey salt precursor.

INTRODUCTION

Dimethyloxosulfonium methylide, prepared by reaction of trimethyloxosulfonium iodide with sodium hydroxide, was first reported by Corey (1) in 1962 and was shown to be a reactive nucleophilic ylid capable of "interacting with the carbonyl function of aromatic and nonconjugated aldehydes and ketones to form oxiranes and with α,β-unsaturated ketones which are Michael receptors to form cyclopropyl ketones." (2,3,4) Since 1965 this reagent or its derivatives have been used to introduce the cyclopropyl group into a variety of tropones and benzotropones producing homo- and benzohomotropones. (5) Our interest in the study of the ^{13}C nmr of the carbonium ions generated from these homo- and benzohomotropones initiated our interest in the introduction of cyclopropyl-^{13}C into the tropones and benzotropones via their reaction with dimethyloxosulfonium methylide-^{13}C.

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In order to obtain the highest yield possible for the preparation of the starting material, trimethyloxosulfonium-^{13}C iodide, an investigation of the reaction used by Corey to prepare this compound was also undertaken. With suitable changes in the ratio of the starting dimethyl sulfoxide and methyl iodide it has been possible to increase the yield of trimethyloxosulfonium iodide from 53.6% originally reported (4) to 77%.

RESULTS AND DISCUSSION

The synthetic scheme used to prepare the trimethyloxosulfonium-^{13}C iodide is summarized in the following reaction sequence:

$$(1)\quad Ba^{13}CO_3 \xrightarrow{H+} {}^{13}CO_2 \xrightarrow{LiAlH_4} {}^{13}CH_3OH \xrightarrow{HI} {}^{13}CH_3I$$

$$(2)\quad {}^{13}CH_3I \ + \ (CH_3)_2SO \longrightarrow (CH_3)_3SOI$$

Synthetic methods were tested using both unlabelled and ^{13}C-labelled barium carbonate. The procedure of Nystrom (6) as modified below for the preparation of $^{13}CH_3OH$ was found to yield 81% of 90% ^{13}C-enriched product. Using the method of Roberts (7) afforded 62% of 90% ^{13}C-enriched $^{13}CH_3I$. Investigation of the reaction of dimethyl sulfoxide and unlabelled methyl iodide showed that varying the ratio of reactants could increase the yield pf trimethyloxosulfonium iodide to 77% as shown in Table I. Using a ratio of 1.5 : 1 unlabelled dimethyl sulfoxide to 90% ^{13}C-enriched $^{13}CH_3I$ afforded 77% of 30% trimethyloxosulfonium-^{13}C iodide.

EXPERIMENTAL

Methanol-^{13}C. The procedure used to prepare this compound was essentially that of Nystrom (6) with the main modification being that sulfuric acid was used to generate $^{13}CO_2$ from the barium carbonate-^{13}C and that the complete reaction sequence was performed on a vacuum line. The product obtained was removed from the vacuum line and redistilled to give 2.6 g (81 mmole, 81% based on barium carbonate-^{13}C) of 90%-enriched methanol-^{13}C; nmr (neat) δ $^{13}CH_3$ consists of a doublet centered at 3.31 ppm (J_{CH} = 140 Hz) for 90%-enriched $^{13}CH_3OH$ and a singlet for $^{12}CH_3$ at 3.31 ppm for 10%-unlabelled $^{12}CH_3OH$. The OH

Table I

Yields of Trimethyloxosulfonium Iodide Obtained With Varying Ratios[a] of Starting Materials[b]

$(CH_3)_2SO$			$(CH_3)_3SOI$		
ml	g	mmole	g	mmole	Yield, %
4.5	4.95	63.4	4.2	19.1	30.3
5.4	5.94	76.0	8.5	38.6	55.9
6.0	6.60	84.5	10.0	45.4	65.9
6.5	7.15	91.5	10.8	49.1	71.1
7.0	7.70	98.6	11.4	51.8	75.1
7.5	8.25	105.6	11.7	53.2	77.0
8.0	8.80	112.6	11.5	52.3	75.7
8.5	9.35	119.7	10.3	46.8	67.8
9.0	9.90	126.7	8.8	39.9	57.9
9.5	10.45	133.8	7.2	32.7	47.4
10.0	11.00	140.8	5.5	24.9	36.2
11.0	12.10	154.9	3.4	15.4	22.4
12.0	13.20	168.9	2.8	12.7	18.4
15.0	16.50	211.2	2.2	9.9	14.5

[a] The amount of methyl iodide used was held constant at 4.3 ml (9.8 g, 69 mmole) throughout all the runs reported. [b] All the results reported are the average of three consecutive reactions where the yields of each agreeded within 1%.

proton for both species appeared at 4.2 ppm.

Methyl-^{13}C Iodide. The procedure used to prepare this compound is essentially that used by Roberts (7) for the preparation of $^{14}CH_3I$. This procedure afforded 7.1 g (50 mmole, 62%) of 90%-enriched product, bp 40-41° (760 mm); nmr (CCl_4) δ $^{13}CH_3$ doublet centered at 2.20 ppm (J_{CH} = 152Hz) for 90%-enriched $^{13}CH_3I$ and a singlet for $^{12}CH_3I$ at 2.20 ppm for 10% $^{12}CH_3I$.

Anhydrous Dimethyl Sulfoxide. Dimethyl sulfoxide (Matheson, Colemen and Bell) was stirred overnight over powdered calcium hydride and then distilled under reduced pressure, bp 64-65° (4 mm). The resulting anhydrous dimethyl sulfoxide was used immediately.

Trimethyloxosulfonium-^{13}C Iodide. This compound was prepared by the method of Corey (4) but using different ratio of reactants. A solution of 7.5 ml (8.25 g, 105.6 mmole) of anhydrous dimethyl sulfoxide and 4.3 ml (9.8 g, 69 mmole) of methyl iodide (90%-enriched ^{13}C) was placed into a 15 ml one-necked round-bottomed flask equipped with a condenser and a nitrogen inlet tube attached to the top of the condenser. The other end of the nitrogen tube was connected to a mercury-sealed U-tube to which the system was opened. This mixture was refluxed under nitrogen for 24 hrs during which time a yellowish-brown solid precipitated. The solid was filtered and washed with 20 ml of cold tetrahydrofuran and then air dried to give 11.7 g (53.2 mmole, 77%) of fine white crystals of trimethyloxosulfonium iodide (30%-enriched ^{13}C), mp 176-177°; nmr (d_6-DMSO) δ $(^{13}CH_3)_3$ consists of a doublet centered at 3.90 ppm (J_{CH} = 145-146 Hz) for 30% $(^{13}CH_3)_3SOI$ and a singlet for $(^{12}CH_3)_3$ at 3.90 ppm for 70% $(^{12}CH_3)_3SOI$.

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